Time-Resolved IR Spectroscopy Reveals a Mechanism with TiO2 as a Reversible Electron Acceptor in a TiO2 – Re Catalyst CO2 Photoreduction System

Mohamed Abdellah, Ahmed M. El-Zohry, Liisa J. Antila, Christopher D. Windle, Erwin Reisner, and Leif Hammarström

J. Am. Chem. Soc., Just Accepted Manuscript • Publication Date (Web): 24 Dec 2016

Downloaded from http://pubs.acs.org on December 26, 2016

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.
Time-Resolved IR Spectroscopy Reveals a Mechanism with TiO₂ as a Reversible Electron Acceptor in a TiO₂—Re catalyst CO₂ Photoreduction System

Mohamed Abdellah a,b*, Ahmed M. El-Zohry a, Liisa J. Antila a, Christopher D. Windle c, Erwin Reisner c, and Leif Hammarström a*

a Ångström Laboratory, Department of Chemistry, Uppsala University, Box 523, 75120 Uppsala, Sweden
b Department of Chemistry, Qena Faculty of Science, South Valley University, 83523 Qena, Egypt
c Christian Doppler Laboratory for Sustainable SynGas Chemistry, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, U.K.

KEYWORDS: CO₂ photo-catalytic reduction, fs and ns time resolved IR spectroscopy, TEOA, Re molecular catalyst, and photo-catalytic mechanism

ABSTRACT: Attaching the phosphonated molecular catalyst [ReBr(bpy)(CO)₃][L] to the wide-band gap semiconductor TiO₂ strongly enhances the rate of visible-light driven reduction of CO₂ to CO in dimethyl formamide (DMF) with triethanolamine (TEOA) as sacrificial electron donor. Herein, we show by transient mid-IR spectroscopy that the mechanism of catalyst photoreduction is initiated by ultrafast electron injection into TiO₂, followed by rapid (ps-ns) and sequential two-electron oxidation of TEOA that is coordinated to the Re center. The injected electrons can be stored in the conduction band (CB) of TiO₂ on a ms-s time scale, and we propose they lead to further reduction of the Re-catalyst and completion of the catalytic cycle. Thus, the excited Re catalyst gives away one electron and would eventually get three electrons back. The function of an electron reservoir would represent a role for TiO₂ in photo-catalytic CO₂ reduction that has previously not been considered. We propose that the increase in photocatalytic activity upon heterogemisation of the catalyst to TiO₂ is due to the slow charge recombination and the high oxidative power of the Re²⁺ species after electron injection, as compared to the excited MLCT state of the unbound Re catalyst or when immobilized on ZrO₂, which results in a more efficient reaction with TEOA.

INTRODUCTION

Tremendous efforts have been made to explore new energy resources in order to face the problems of energy shortage and global warming. Continuous increase of the CO₂ concentration in the atmosphere is the main reason behind global warming. A smart solution is to convert CO₂ emissions to fuels or other useful chemicals, which is one of the goals of artificial photosynthesis. Photocatalytic and photoelectrocatalytic reduction of CO₂ has been achieved by employing metals and semiconductors or enzymes bound to photoelectrodes. The former suffers from poor selectivity and, in contrast, the latter shows excellent selectivity but suffers from stability issues. Balancing between both high selectivity and stability can potentially be achieved using synthetic molecular catalyst for CO₂ reduction. Generally, there are two approaches to CO₂ photoreduction with synthetic molecular catalysts. In the first one, the catalyst receives electrons from a photosensitizer after the excitation. In the second approach, the catalyst itself plays a dual role, working as both photosensitizer and catalyst, as exemplified by the rhenium tricarbonyl bipyridine bromide [ReBr(bpy)(CO)₃]⁺ catalyst. Recently, some of us attached this catalyst to an n-type TiO₂ semiconductor via phosphonic acid linker groups (TiO₂—[Re(2,2’-bipyridine-4,4’-bisphosphonic acid)(CO)₃(L)], where initially L = Br⁻ but is replaced during the photocatalysis; Scheme 1). In the presence of triethanolamine (TEOA as electron donor this led to a higher yield (TON) of CO₂ photoreduction compared to both the homogenous system without TiO₂ and to systems where the same catalyst was attached to other metal oxides, such as ZrO₂. TiO₂ was proposing to stabilized reduced catalyst intermediates and hinder formation of unreactive Re-Re dimers, but not participate directly in the electron transfer reactions.

In the present study we attempt to answer several questions, in order to understand the role of TiO₂ and to propose the photoreduction mechanism of the attached catalyst. First, is TiO₂ unreactive or is the excited [ReBr(bpy)(CO)₃] oxidized by electron injection into TiO₂ as has been shown in some cases? Second, what are the roles of the TEOA in the photocatalytic process? Finally, what is the role of TiO₂ in the photoreduction process? To answer these questions we used time-resolved IR (TRIR) in the region of CO stretching vibrations, from time scales of femtosecond up to seconds. The ν(CO) is very sensitive to the electron density of the central Re ion, allowing us to identify and follow the Re excited state and different oxidation states.

EXPERIMENTAL SECTION

Steady-state spectroscopy. Steady-state absorption and emission were recorded using a Varian Cary 5000 and a Horiba Jobin Yvon Fluorolog, respectively. The emission spectrum for
Electron injection from excited \([\text{Re}^0(\text{bpy})(\text{CO})_3\text{DMF}]^+\) to TiO\(_2\):

To investigate the electron injection from the excited catalyst \([\text{Re}^0(\text{bpy})(\text{CO})_3\text{DMF}]^+\) to TiO\(_2\), first we used the same sensitization conditions to attach the catalyst to ZrO\(_2\) (non-injecting semiconductor as a reference).\(^{23}\) Then we used fs-TRIR to test the electron injection process. The ZrO\(_2\)--\([\text{Re}^0(\text{bpy})(\text{CO})_3\text{DMF}]^+\) system shows the typical spectral features of the excited \([\text{Re}^0(\text{bpy})(\text{CO})_3]^+\): the bleach of the ground state CO bands (GSB) at ~2040 cm\(^{-1}\) and around 1960 cm\(^{-1}\) and the corresponding excited-state bands (ESA) at ~2057 cm\(^{-1}\) and around 2010 cm\(^{-1}\) (Figure 1A).\(^{24}\) In addition to these spectral features, the TiO\(_2\)--\([\text{Re}^0(\text{bpy})(\text{CO})_3\text{DMF}]^+\) system shows: i) a new peak on the higher wavenumber side compared to the ground state bleach (GBS) due to the oxidized state of the catalyst,\([\text{Re}^0(\text{bpy})(\text{CO})_3\text{DMF}]^+\) (at 2088 cm\(^{-1}\)) ii) a broad absorption band in the entire probe region due to electrons in the TiO\(_2\) conduction band (CB) \([\text{Re}^0(\text{bpy})(\text{CO})_3\text{DMF}]^+\) (Figure 1B). The amplitude of both the oxidized catalyst \([\text{Re}^0(\text{bpy})(\text{CO})_3]^+\) peak and the electrons in the TiO\(_2\) CB increase with increasing delay time with no decay up to 5 ns. Thus, there is no observable charge recombination on this time scale, but instead a slow additional component of electron injection. The traces at 2088 cm\(^{-1}\) (oxidized catalyst after back ground subtraction of \(\varepsilon_{\text{CB}}\) signal) and at 2125 cm\(^{-1}\) (\(\varepsilon_{\text{CB}}\) signal) have different kinetics (Figure S2B). The electron trace shows significant appearance of the \(\varepsilon_{\text{CB}}\) signal on a ~2 ps time scale, while the oxidized catalyst peak growth is slower (~30 ps). This difference could be because the electron signal is very strong and initially buries the oxidized catalyst peak. The catalyst peak is initially broad but narrows with time, and is thus more clearly seen, as has been observed before.\(^{22,23}\) The spectral narrowing occurs on ~30 ps time scale. In separate experiments using ns-laser excitation with a cw-IR laser probe (see Experimental section), we found that the electrons recombine on the tens of ps time scale (Figure S2A).

The role of TEOA: TEOA is not just an external (outer-sphere) electron donor in DMF solutions. Instead, under illumination in the presence of TEOA the \([\text{Re}^0(\text{bpy})(\text{CO})_3\text{DMF}]^+\) catalyst binds CO\(_2\) in the form of a TEOA-CO \(_2\) carbonate ligand \([\text{Re}^0(\text{bpy})(\text{CO})_3\text{OC(O)}\text{O}-(\text{CH}_2)_2\text{NR}_2]^+\) (Scheme 1). Ishitani and coworkers showed the analogous ligand exchange process for the homogeneous \([\text{Re}^0(\text{bpy})(\text{CO})_3\text{DMF}]^+\) catalyst in the presence of TEOA and CO\(_2\) by using FTIR and ESI-MS measurements.\(^{25}\) Based on their findings and FTIR spectra, we could confirm the formation of TiO\(_2\)--\([\text{Re}^0(\text{bpy})(\text{CO})_3\text{OC(O)}\text{O}-(\text{CH}_2)_2\text{NR}_2]^+\) under irradiation in the presence of TEOA and CO\(_2\) (Figure S3A, S3C and scheme 1). Fs-TRIR spectroscopy shows that also after ligand exchange the new species \([\text{Re}^0(\text{bpy})(\text{CO})_3\text{OC(O)}\text{O}-(\text{CH}_2)_2\text{NR}_2]^+\) is able to inject electrons to TiO\(_2\) (Figure S3B and STD). The ultrafast electron injection has the same amplitude with and without TEOA and CO\(_2\) indicating that the injecting species is the major species (Figure S3E).

Moreover, we found that for TiO\(_2\)--\([\text{Re}^0(\text{bpy})(\text{CO})_3\text{OC(O)}\text{O}-(\text{CH}_2)_2\text{NR}_2]^+\) the oxidized catalyst TRIR peak on the high wavenumber side of the GSB is absent, while the electrons are clearly present in the CB of TiO\(_2\). Thus, the TEOA-ligand seems to be able to reduce the oxidized catalyst on the same time scale as the electron injection process, forming the species where the “hole” has moved to the TEOA ligand: TiO\(_2\)--\([\text{Re}^0(\text{bpy})(\text{CO})_3\text{OC(O)}\text{O}-(\text{CH}_2)_2\text{NR}_2]^+\). The FTIR spectra of TiO\(_2\)--\([\text{Re}^0(\text{bpy})(\text{CO})_3\text{OC(O)}\text{O}-(\text{CH}_2)_2\text{NR}_2]^+\) (Figure 1C) shows the TRIR spectra of TiO\(_2\)--\([\text{Re}^0(\text{bpy})(\text{CO})_3\text{OC(O)}\text{O}-(\text{CH}_2)_2\text{NR}_2]^+\) where the e\(_{\text{CB}}\) signal at 2100 cm\(^{-1}\) has been subtracted, to emphasize the molecular signals. The CO signals of TiO\(_2\)--\([\text{Re}^0(\text{bpy})(\text{CO})_3\text{OC(O)}\text{O}-(\text{CH}_2)_2\text{NR}_2]^+\) are upshifted compared to the ground state complex, consistent with formation of a cation radical in the vicinity of the Re\(^{\text{II}}\) center. We note that the spectra
are similar to those of the \((\text{bpy})\text{Re}^{II}\) MLCT state on ZrO2, but they are more narrow and do not show the same shift with time as the MLCT state on ZrO2. For TiO2 sample the peak stabilizes at 2036±1 cm\(^{-1}\) within 1 ps while the ZrO2 sample red-shifts by 10 cm\(^{-1}\) during 500 ps (see Figure S4). The signal of TiO2(e\(^-\))—\([\text{Re}(\text{bpy})(\text{CO})_3\text{OC(O)}\text{O}(\text{CH}_2\text{N}^+\text{R}_2)]\) should therefore not be mistaken for an MLCT state.

![Figure 1](image1)

**Figure 1.** A) fs-TRIR for the ZrO\(_2\)--\([\text{Re}^{I}(\text{bpy})(\text{CO})_3\text{DMF}]^\text{+}\) system in DMF, B) fs-TRIR for the TiO\(_2\)--\([\text{Re}^{I}(\text{bpy})(\text{CO})_3\text{DMF}]^\text{+}\) system without TEOA, and C) fs-TRIR for the TiO\(_2\)--\([\text{Re}^{I}(\text{bpy})(\text{CO})_3\text{OC(O)}\text{O}(\text{CH}_2\text{N}^+\text{R}_2)]\) system in DMF/TEOA solution (5:1) and CO\(_2\) bubbling (the absorption at 2100 cm\(^{-1}\) was subtracted from the spectra to emphasize molecular signals).

The reactions were followed on a longer time scale using a ns-laser/TRIR setup. Figure 2 compared the TRIR spectra of TiO\(_2\)--\([\text{Re}^{I}(\text{bpy})(\text{CO})_3\text{DMF}]^\text{+}\) without (2A) and with (2B) TEOA and CO\(_2\). At first sight, in figure 2A, we can recognize the GSB peak and the oxidized catalyst peak TiO\(_2\)(e\(^-\))—\([\text{Re}^{II}(\text{bpy})(\text{CO})_3\text{DMF}]^{2+}\) on the higher wavenumber side, which agrees very well with the fs-FTIR results of Figure 1A. These signals decay on a time scale of a few μs. In contrast, after introducing TEOA and CO\(_2\), we found that, in addition to the GSB of TiO\(_2\)(e\(^-\))—\([\text{Re}^{I}(\text{bpy})(\text{CO})_3\text{OC(O)}\text{O}(\text{CH}_2\text{N}^+\text{R}_2)]\) at 2020 cm\(^{-1}\), an absorption peak appears on the lower wavenumber side, and this grows stronger during the first few 100’s of ns. This means an increased electron density on the Re center, and can be attributed to a singly reduced catalyst.34,35 Our assignment is based on the following spectral analysis. We subtract the spectrum at 50 ns from the spectrum at .org/10.1021/ic102324p</url></related-urls></urls><electronic-
Figure 2, A) ns-TRIR spectra at different time delays after the photo-excitation for A) TiO$_2$–[Re I(bpy)(CO)$_3$DMF]$^+$, and B) TiO$_2$–[Re I(bpy)(CO)$_3$] in the presence of TEOA/CO$_2$. The molecular GSB is at 2040 and 2025 cm$^{-1}$, respectively, in agreement with FTIR spectra. Panel B marks also the peak at 2015 cm$^{-1}$ for the singly reduced catalyst TiO$_2$(e$^-$)–[ReI(bpy$^-$)(CO)$_3$OC(O)O-CH$_2$CHN$^+$R$_2$]$^0$.

In the absence of TEOA/CO$_2$ most of the signal from CB electrons in TiO$_2$ decays within 10 µs, by charge recombination with the oxidized catalyst: TiO$_2$(e$^-$)–[ReII(bpy)(CO)$_3$DMF]$^{2+} \rightarrow$ TiO$_2$–[Re I(bpy)(CO)$_3$DMF]$^+$. In the sample with TEOA/CO$_2$, instead, the electrons in the TiO$_2$ CB do not show any decay up to tens of ms (Figures 3A and 3B). From the transient spectra and traces it is clear that the reduced catalyst [Re(bpy$^-$)(CO)$_3$OC(O)[OC(OC(OCO)CH$_2$CHN$^+$R$_2$)]$^0$ forms on a rapid time scale $\tau_1 = 35$ ns followed by a slow rise in Figure 3A ($\tau_2 = 1.8$ µs). At the same time the background signal of CB electrons increases for which the IR extinction coefficient is larger than for the catalyst species (cf. the relative $\Delta$Abs of the molecular peak vs. broad background in Figure 2B).

**TiO$_2$ role in CO$_2$ photoreduction by [Re(bpy)(CO)$_3$]$^+$ catalyst:**

The data indicate that there is an electron injection from the excited [Re(bpy)(CO)$_3$L]$^*$ to the TiO$_2$ CB on the ps time scale. For the sample with TEOA/CO$_2$ this leads to phototriggered oxidation of TEOA and formation of a reduced catalyst, which is not seen on ZrO$_2$. Therefore, TiO$_2$ has an active role in the light induced electron transfer reactions of this system. To further investigate the role of TiO$_2$ we probed the destiny of CB electrons on longer time scales.

Figure 3, A) traces at 2015 cm$^{-1}$ for TiO$_2$-catalyst (red) and for TiO$_2$-catalyst in the presence of TEOA and CO$_2$ (black) up to 10 µs (inset: showing the rising component), and B) traces at 2100 cm$^{-1}$ (electrons in the TiO$_2$ CB) for TiO$_2$-catalyst (red) and TiO$_2$-catalyst in the presence of TEOA/CO$_2$ (black) up to 1.5 sec. delay after the photo-excitation.

Figure 3B compares the traces at 2100 cm$^{-1}$ (CB electron absorption region) up to 1.5 seconds after photo-excitation of the TiO$_2$-catalyst without (red trace) and with introducing TEOA/CO$_2$ (black trace). Without TEOA/CO$_2$ no electrons are left in the TiO$_2$ CB on this time scale, but introduction of TEOA and CO$_2$ to the attached catalyst changes the kinetics drastically. Clearly, the electrons are still in the TiO$_2$ CB on this time scale and only around 50% of the electrons had disappeared from the CB after around 100 ms, while the remaining 50% decays with $\tau \sim 1$ s.

This time scale ($\tau \sim 1$ s) is very similar to what was reported for decay of the reduced catalyst signal ($\tau = 0.4$ s) at 500 nm (bpy-ReI$^-$ signal) 21 even though we could not follow the molecular signal by mid IR on the ms to seconds time scale. It is important to note that there is no accumulation of more reduced catalyst species upon repeated laser flashing or continuous irradiation. Thus, we propose that the CB electrons are added to the reduced catalyst, and lead to catalytic turnover, restoring the sample to the initial TiO$_2$–[Re(bpy)(CO)$_3$OC(OC(OCO)CH$_2$CHN$^+$R$_2$)]$^0$ state; we discuss a possible mechanism in the next section. At present we do not know if the CB electrons that decay with $\tau \sim 89$ ms also contribute to catalyst reduction, or if they are lost in side reactions. In any case, these experiments add more evidence that TiO$_2$ plays a role in the photocatalytic reduction of CO$_2$ in this system other than being a scaffold. In this context, we note again that formation of the singly reduced catalyst [Re(bpy$^-$)(CO)$_3$]$^-$...
Proposed photocatalytic mechanism: The mechanism of CO$_2$ reduction by [Re(bpy)(CO)$_3$L]$_2$ catalysts is still under debate, with different mechanistic pathways being discussed. Under electro-catalytic reduction conditions, the complex typically undergoes a two-electron reduction and loses the labile ligand (L) to form a [Re(bpy)(CO)$_3$] species that binds to CO$_2$ and enters the catalytic cycle. However, under photo-catalytic reduction conditions, already the one-electron-reduced complex [Re(bpy)(CO)$_3$] may bind to CO$_2$ and start the catalytic cycle. Attaching the catalyst to TiO$_2$ improves the catalytic activity but it also increases the mechanistic complexity further. Scheme 2 presents our proposed mechanism of the photo-catalytic reduction of CO$_2$ using TiO$_2$—[Re(bpy)(CO)$_3$]DMF\textsuperscript{7} system in the presence of TEOA/CO$_2$ in DMF solution. As shown above TiO$_2$—[Re(bpy)(CO)$_3$] is able to capture CO$_2$ and bind it as a carbonated TEOA ligand, forming the catalyst TiO$_2$—[Re(bpy)(CO)$_3$]OC(O)-CH$_2$CH$_2$N$^+$R$_2$-CO$_2$. Upon photoexcitation of this complex, electron injection into the CB of TiO$_2$ occurs on the ps time scale. This is rapidly followed by electron transfer from the bound TEOA ligand to the oxidized catalyst to form TiO$_2$(e$^-$)—[Re(bpy)(CO)$_3$]OC(O)-CH$_2$CH$_2$N$^+$R$_2$.\textsuperscript{9} On a ps-ns time scale the (+CH$_2$CH$_2$N$^+$R$_2$)$_2^{+}$ radical cation shifts the radical from the nitrogen to an adjacent carbon, that deprotonates, and donates a second electron to further reduce the complex and form TiO$_2$(e$^-$)—[Re(bpy)(CO)$_3$]OC(O)-CH$_2$CH$_2$N$^+$R$_2$$^+$ + H$. This must be followed by release of the oxidized TEOA to form the CO$_2$-bound catalyst TiO$_2$(e$^-$)—[Re(bpy)(CO$_3$)]$_2$.\textsuperscript{10} The CO$_2$ carbon now coordinates to the Re center and two reducing equivalents are located on the CO$_2$ group. The CO$_2$ may be derived from the carbonate-TEOA ligand that loses TEOA and rearranges to carbon coordination. Alternatively, the entire ligand decoordinates to form the one-electron-reduced, 17-electron species TiO$_2$(e$^-$)—[Re(bpy)(CO)$_3$]$^+$ that then binds another CO$_2$ molecule. Both pathways end up forming the critical TiO$_2$(e$^-$)—[Re(bpy)(CO)$_3$]$_2$ species. On a time scale of milliseconds to seconds, electrons in the CB of TiO$_2$ reduce [Re(bpy)(CO)$_3$]$_2$ to form the metallacarboxylate intermediate species TiO$_2$—[Re(bpy)(CO)$_3$]$_2$. The metallacarboxylate intermediate can undergo a protonation (from TEOA/DMF) followed by loss of H$_2$O to generate TiO$_2$—[Re(bpy)(CO$_3$)]$^+$.\textsuperscript{2} This 18-electron species must be reduced before CO is released and the starting complex is regenerated. The question is where does this final electron come from under our experimental conditions. Based on results from Kubiat and coworkers\textsuperscript{5}, we suggest that a small fraction of a electron equivalents, from the TiO$_2$ CB, could catalytically reduce the entire population of [Re(bpy)(CO)$_3$]$.^+$. Kubiat and coworkers found that sub-stoichiometric amounts (~0.1 eqs) of reductant was sufficient to convert an entire sample of [Re(bpy)(CO)$_3$] to [Re(bpy)(CO$_3$)DMF] in homogeneous solution. They presented a mechanism with an electron-transfer-catalyzed ligand exchange.\textsuperscript{3} Formation of TiO$_2$—[Re(bpy)(CO$_3$)]$^+$ in a small amount leads to replacement of CO with solvent molecule (DMF) to form TiO$_2$—[Re(bpy)(CO$_3$)DMF]. This complex is more reducing than the CO-complex and therefore undergoes electron transfer with TiO$_2$—[Re(bpy)(CO$_3$)]$^+$ to propagate the reduction-ligand exchange process, according to the small loop presented in Scheme 2.\textsuperscript{3} Finally, TiO$_2$—[Re(bpy)(CO$_3$)DMF] binds TEOA and CO$_2$ to reform the starting material, as it was before laser flash initiation. Note that the scheme does not indicate all possible charge recombination steps and other loss pathways, which presumably make the overall yield much less than 100%. The most interesting part of the proposed mechanism is that the catalyst is able to inject electrons to TiO$_2$, and when the catalyst becomes reduced by TEOA it can accept the electron back. This explain the redox active role of TiO$_2$ as an electron reservoir in TiO$_2$—catalyst system in presence of TEOA and CO$_2$.
Supporting Information.
steady-state absorption, emission and IR, and complementary
time-resolved IR spectroscopic data. This material is available
free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*Prof. Leif Hammarström
(Leif.Hammarstrom@kemi.uu.se)

*Dr. Mohamed Abdellah
(Mohamed.Genawy@kemi.uu.se)

Notes
The authors declare no competing financial interests.

ACKNOWLEDGMENT

The authors are grateful for funding from the Knut and Alice
Wallenberg Foundation, the Swedish Energy Agency, the
Swedish Research Council, the Austrian Christian Doppler
Research Association (Austrian Federal Ministry of Science,
Research and Economy and the National Foundation for
Research, Technology and Development) and the OMV Group.
Dr. Mohammad Mirmohades, Jens Föhlinger and Luca D’Amaro
are acknowledged for their help with fs-TRIR and ns-FTIR. Prof.
Sascha Ott is also acknowledged for his helpful discussion.
We are dedicating this work to the soul of Prof. Ahmed Zewail.

REFERENCES

(1) Field, C.B., V.R. Barros, D.J. Dokken, K.J. Mach, M.D.
Mastrandrea, T.E. Bilir, M. Chatterjee, K.L. Ebi, Y.O. Estrada, R.C.
Genova, B. Girma, E.S. Kissel, A.N. Levy, S. MacCarron, P.R.
Mastrandrea, and L.L. White (eds.), Climate Change 2014: Impacts,
Cambridge University Press, Cambridge, United Kingdom and New York, NY,
USA, 2014.

(2) Riplinger, C.; Sampson, M. D.; Ritzmann, A. M.; Kubiak,

Leeuw, N. H. USA, University Press, Cambridge, United Kingdom and New York, NY,
Cambridge

(4) Takeda, H.; Koike, K.; Inoue, H.; Ishitani, O.

Thauer, R. K.; Waldrop, G. L.; Ragsdale, S. W.; Dupuis, M.; Ferry, J. G.; Fujita, E.; Hille, R.; Kenis, P.

(6) Figueiredo, M. C.; Ledezma-Yanez, I.; Koper, M. T. M.

(7) Sahara, G.; Ishitani, O.


(9) Windle, C. D.; Campian, M. V.; Duhme-Klair, A.-K.;

(10) Windle, C. D.; Perutz, R. N.

(11) Li, C. W.; Kanan, M. W.

Fortmeyer, I. C.; Park, J. E.; Zhang, T.; Liao, K.; Gu, J.; Yan, Y.;
Shaw, T. W.; Abelev, E.; Bocsarly, A. B.

(13) Woolerton, T. W.; Sheard, S.; Reisner, E.; Pierce, E.;
Ragsdale, S. W.; Armstrong, F. A.

(14) Woolerton, T. W.; Sheard, S.; Pieres, E.; Ragsdale, S. W.;
Armstrong, F. A.

(15) Mambeck, G. F.; Muckerman, J. T.; Szalda, D. J.; Himeda,
yFujita, E.

(16) Aragaw, J.; Fujita, E.; Scharfe, H. F.; Muckerman, J. T.

(17) Kumar, B.; Llorente, M.; Trochlich, J.; Dang, T.; Sathrum,
A.; Kubiak, C. P.

(18) Pastor, E.; Pesci, F. M.; Reynal, A.; Handoko, A. D.; Guo,
M.; An, X.; Cowan, A. J.; Klug, D. R.; Durrant, J. R.; Tang, J.

(19) Hawecker, J.; Lehn, J.-M.; Ziesssel, R.

(20) Windle, C. D.; Pastor, E.; Reynal, A.; Whitwood, A. C.;
Vaynzof, Y.; Durrant, J. R.; Perutz, R. N.; Reisner, E.

(21) She, C.; Guo, J.; Lian, T.

(22) Nahhas, A. E.; Cinnizzou, A.; Mourik, F. V.; Blancone-
Rodriguez, A. M.; Záliš, S.; Vlček, J. A.; Chergui, M.

(23) El Nahhas, A.; Consani, C.; Blanco-Rodriguez, A. M.;
Lan caster, K. M.; Braem, O.; Cinnizzou, A.; Towrie, M.; Clark, I. P.;
Záliš, S.; Chergui, M.; Vlček, A.

(24) Asbury, J. B.; Hao, E.; Wang, Y.; Lian, T.

Fernandes, D. L. A.; Sa, J.

Hammarström, L.; Lomoth, R.

(27) Mirmohades, M.; Adamska-Venkatesh, A.; Sommer, C.;
Reijerse, E.; Lomoth, R.; Lubitz, W.; Hammarström, L.

(28) Kirgan, R. A.; Sullivan, B. P.; Rillena, D. P.

Imori, D.; Ishitani, O.

(30) Wang, Y.; Asbury, J. B.; Lian, T.

(31) Anderson, N. A.; Lian, T.

(32) Anderson, N. A.; Ai, X.; Lian, T.

(33) Smieja, J. M.; Kubiak, C. P.

(34) Grice, K. A.; Gu, X. X.; Sampson, M. D.; Kubiak, C. P.

(35) Reithmeier, R.; Bruckmeier, C.; Rieger, B.
Catalysts 2012, 2, 544.

(36) Takeda, H.; Koike, K.; Inoue, H.; Ishitani, O.

(37) Amouyel, E.

(38) Lehn, J. M.; Sauvage, J.; GAUTHIER-VILLARS 120

Tachibana, H.; Inoue, H.

(40) Sampson, M. D.; Froehlich, J. D.; Smieja, J. M.; Benson,
E. E.; Sharp, I. D.; Kubiak, C. P.

(41) Schneider, T. W.; Ertem, M. Z.; Muckerman, J. T.;
Angelas-Boza, A. M.

(42) Schneider, T. W.; Ertem, M. Z.; Muckerman, J. T.;
Angelas-Boza, A. M.